

Amorphous Mineral Colloids of Soils of the Pacific Region and Adjacent Areas¹

YOSHINORI KANEHIRO² and LYNN D. WHITTIG³

THE PRESENCE of amorphous mineral colloids in soils and geologic formations is not as uncommon as was first believed in the early years following the acceptance of the clay mineral concept. In the early reports the occurrence of amorphous material was associated with only a few rare and isolated clay materials. Because amorphous colloids are not the major component in most soils and their presence may be found in relatively low concentrations, if found at all, their detection has been difficult. Moreover, whereas crystalline clay minerals are relatively uniform in composition, the amorphous materials exhibit a varying degree of composition and poor degree of crystallinity, further adding to the difficulty in their identification. Often their presence has been suggested only because mineral allocations of crystalline materials failed to add up to 100 per cent. In recent years improvement in the use of techniques such as X-ray diffraction, infrared absorption, electron microscopy, and surface area determination, has made it possible to make significant progress in the study of amorphous colloids.

Much of the research dealing with amorphous mineral colloids in soils has been conducted by soil scientists working in the Pacific region or in its adjacent areas. The leadership in this field definitely belongs to this group of researchers. It is the object of this paper to review and discuss the contributions of these workers in order to obtain a better perspective of this very important fraction of soils. These investigators

have pointed out that the amorphous constituents make up a sizeable fraction in many soils occurring in Hawaii, Japan, New Zealand, Oregon, and other Pacific areas. These amorphous mineral colloids play a prominent role in soil formation and also impart certain distinctive and unique properties to the soil. Thus, a review of this nature appears justified.

NOMENCLATURE OF AMORPHOUS COLLOIDS

The isolation and description of amorphous colloids have been difficult because of the great variability in materials. Moreover, early samples classified as "amorphous" were actually found to be finely crystalline with modern X-ray diffraction methods. Stromeier and Hausmann first used the name allophane to describe amorphous material lining cavities in marl in 1816. Since that time many related materials have been called allophane and this term has become associated with amorphous constituents of clay. Ross and Kerr (1934) described allophane as essentially an amorphous solid solution of silica, alumina, and water having no definite atomic structure, and they applied the term allophane to a great number of amorphous clay materials regardless of their composition. They studied five specimens of allophane, all essentially hydrous aluminum silicates, and found that SiO_2 ranged from 25 to 34 per cent, Al_2O_3 from 30 to 36 per cent, and H_2O from 31 to 38 per cent. The New Zealand workers (Fieldes *et al.*, 1952, 1954; Birrell and Gradwell, 1956) have used the term amorphous colloidal hydrous oxides apart from the term allophane in their description of amorphous clays. With allophane, which is considered to be one of the most important amorphous minerals, Fieldes (1955, 1956) has preferred to recognize three distinct

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² Department of Agronomy and Soil Science, University of Hawaii, Honolulu.

³ Department of Soils and Plant Nutrition, University of California, Davis, California.

forms: allophane A, allophane B, and the intermediate form, allophane AB. In classifying the clay minerals Grim (1953) has included only the allophane group under the amorphous clay minerals. Brown (1955) in his proposed nomenclature has divided the amorphous minerals into oxides, silicates, and phosphates. In this system, allophane is included in the silicates.

OCCURRENCE OF AMORPHOUS COLLOIDS

Kelley and Page (1943) in their mineralogical investigation encountered two soils from Naalehu and South Point on the island of Hawaii that exhibited very high cation exchange capacities, 120 m.e. and 88 m.e. per 100 g., respectively. They reported that differential thermal analysis showed pronounced endothermic peaks at 160° C. for these two soils in addition to showing weak X-ray diffraction patterns. These investigators, therefore, concluded that the high cation exchange properties were related to the presence of considerable amorphous material. Included in this study were soils from Vale, Oregon, and the Mojave Desert, which also gave very indistinct X-ray lines and showed low temperature breaks, inferring the presence of amorphous material.

Dean (1947) in his D.T.A. study of a number of Hawaiian soils derived from ash and lava found that many of these soils contained almost no crystalline clay minerals. In addition some showed almost no hydrous oxides. It was previously shown by Ayres (1943) that some of these same soils possess very high inorganic cation exchange capacities. Dean concluded that it was possible that some of these soils contain alterations of the kaolin minerals.

Tanada (1950) divided Hawaiian soils into five groups on the basis of chemical analyses and dehydration studies. He obtained similar high cation exchange capacity values for the two soils, Naalehu and South Point, that Kelley and Page (1943) had previously reported. However, Tanada did not draw any conclusions regarding the cause of such high values.

Tamura, Jackson, and Sherman (1953) employed X-ray, chemical, thermal, and infrared techniques and found up to 30 per cent allophane in the less than 0.2 micron fraction of

two hydrol humic latosols from the island of Hawaii. The authors noted that the allophane found in the subsoil of one of these soils was very similar to allophane from Woolwich, England (Kerr, 1951). Gibbsite and goethite were reported to make up the bulk of the remaining clay fraction. They also investigated the low humic latosols and reported that the dominant minerals are of the kaolin family. Up to 10 per cent allophane was found to occur in the clay fraction of this group of soils.

In a subsequent paper (1955) the same authors reported on a humic ferruginous latosol from the island of Maui which showed that almost 30 per cent of the clay fraction in the subsoil was composed of allophane.

The occurrence of allophane in some soils of northwestern Oregon was suggested by Whittig *et al.* (1957). These soils, members of the Cascade and Powell series, contained relatively high percentages of alkali-soluble silica and alumina. The amorphous aluminosilicate in these soils was formed by weathering of aeolian volcanic ash.

In earlier work, Whittig (1954) reported the occurrence of a more stable form of allophane in two humic ferruginous latosols of Hawaii. The allophane of these soils had a relatively low cation exchange capacity (of the order of 10 m.e. per 100 g.) and resisted solution in boiling Na_2CO_3 solution.

More recently Bates (1961) described the presence of mineral gels in Hawaiian soils which are mixtures of aluminum, iron, silica, and titanium compounds. The gel material is very reactive chemically and gives rise to inorganic and organomineral complexes in the colloid fraction.

Matsusaka and Sherman (1960) have reported that the iron hydroxide and oxide of the amorphous mineral colloid fraction of Hawaiian lateritic soils will form strongly magnetic iron oxides on dehydration. This may help explain the magnetic properties of weathered ferruginous geological formations.

In Japan Sudo (1954), Sudo and Osaka (1952), and Aomine and Yoshinaga (1955) have pointed to allophane as the dominant constituent of Ando soils which are formed from volcanic ash. These soils are characterized by a

low bulk density, a high organic carbon content, and low base saturation. These properties are attributed to the preponderance of allophane. The Ando soils and related types are found associated with the Pacific ring of volcanic activity. These Japanese workers have found that the fine clay fraction of the Ando soils is characterized by being amorphous to X-rays and possesses medium-to-high cation exchange capacities and high phosphate- and ethylene glycol-retention values.

The New Zealanders have also worked extensively on the identification of amorphous constituents. In 1952 Birrell and Fieldes (1952) and Birrell (1952) identified the presence of amorphous material, principally allophane, in soils derived from rhyolitic and andesitic ash. The allophane was found to be present mainly in the clay fraction although it was inferred that it was present to some extent in the silt fraction. These soils were characterized by a high water-holding capacity, high shrinkage, and irreversible drying, characteristics that are strikingly common to many other Pacific region soils dominated by allophane. Birrell (1952) also pointed out that these soils had a waxy appearance and were greasy to the feel, yet they were not unusually sticky. He further noted that associated with nonreversible drying, liquid and plastic limit values were much greater for undried soils than for dried soils.

Later reports, especially by Fieldes and his co-workers (1955, 1956, 1957, 1955), have confirmed that allophane and other amorphous constituents dominate many New Zealand soils derived from volcanic ash and, in some cases, basaltic parent materials. These workers utilized electron microscopy, differential thermal analysis, and infrared absorption extensively in identifying the presence of amorphous constituents.

PEDOGENIC SIGNIFICANCE OF AMORPHOUS COLLOIDS

Ross and Kerr (1934) described allophane as an amorphous hydrous aluminosilicate having no definite chemical composition and that it is commonly associated with halloysite. They were careful to point out that it is not a microscopic mixture of amorphous silica and alumina. Kerr

(1951) offered confirmatory evidence by absorption spectra that allophane is not a mixture of alumina and silica.

Tamura *et al.* (1953) assigned allophane to weathering stage 11 or the gibbsite stage in the weathering sequence of clay-size minerals as presented by Jackson *et al.* (1948). They noted that the trend for increased gibbsite with increased rainfall is very marked in passing from the low humic latosols to the hydrol humic latosols. With this increase in gibbsite is an associated increase in allophane.

A mechanism for the transition of alumina and silica through allophane to kaolin was proposed by Tamura and Jackson (1953). The steps are as follows: (1) amorphous hydrous alumina crystallizes to a gibbsite structure; (2) with partial dehydration, hydroxyls in the gibbsite octahedra are replaced by oxygens of the silica tetrahedra; (3) this process occurs in the presence of silica solutions and continues through entrance of silica between gibbsite sheets, resulting in a cross-linking of silicated octahedral sheets of alumina which corresponds to allophane; (4) kaolinite is formed from allophane on completion of unidirectional bonding through alternate wetting and drying in an acid medium where enough silica is available.

The stable, nonreactive form of allophane reported by Whittig (1954) as a constituent of some humic ferruginous latosols of Hawaii was considered to be a weathering product of halloysite. Electron micrographs of clay fractions of these soils revealed a transition from well-developed halloysite rod structures to spherical, X-amorphous allophane particles. It was suggested that partial removal of silica from the rigid halloysite rods by leaching allowed the rods to curl up in a direction perpendicular to their original curvature. Allophane formed in this way possessed properties quite different from those of the more labile allophane described by Tamura and Jackson (1953) and would occupy a lower position in the weathering sequence of Jackson *et al.* (1948).

More recently Bates (1960) suggested that the development of allophane is a logical stage in the weathering of certain Hawaiian volcanic ash and also in the matrix of rock. In other cases, he indicated that allophane is an inter-

mediate stage in the weathering sequence of halloysite to gibbsite. Bates also reported the formation of gibbsite crystals upon dehydration of amorphous Fe-Al gels. This observation supports Sherman (1957), who reported that crystalline gibbsite aggregates formed when the soils of the Hydrol Humic Latosol group were air dried. These soils have a high content of amorphous mineral colloids which contain a substantial amount of gel material.

Some of the Japanese workers (Sudo, 1954; Sudo and Ossaka, 1952) conclude that allophane precedes halloysite in the weathering sequence from ash to allophane to halloysite. Aomine and Yoshinaga (1955) have also emphasized that the clay fraction of the volcanic ash soils of Kyushu and Hokkaido formed under similar well-drained conditions is predominantly allophane, regardless of differences in temperature, weathering time, vegetation, and ash origin.

The New Zealanders have also tried to properly position the amorphous materials in the weathering sequence. Fieldes and Swindale (1954) have prepared a flow sheet tracing the mechanism of silicate minerals weathering. They have proposed that the nature of the clay constituents of any soil can be predicted if its parent material and weathering stage are known. The amorphous materials occupy a great role in this flow sheet in that it is thought that the primary silicates (aside from the micas) cannot form layer silicates without first passing through an amorphous stage. Clays derived from rhyolitic and andesitic ash pass through the weathering sequence from amorphous hydrous oxides through allophane to meta-halloysite and kaolin. It is believed that many of the Hawaiian soils derived from andesitic ash follow this same sequence.

In an earlier paper Fieldes *et al.* (1952) emphasized that the amorphous hydrous oxides played more than a brief transitory role. They reported some soils of the lower Cook Islands which showed high cation exchange capacity values. These soils were all low in silica, and also allophane was not found to be a constituent in them. They attributed the cation exchange capacity mainly to the amorphous hydrous oxides.

In later papers Fieldes (1955, 1956, 1957) reported enough fundamental differences in allophane to warrant recognizing three types: allophane A, allophane B, and the intermediate type, allophane AB. Based mainly on infrared absorption data, it was found that silica is linked with alumina to form allophane A while some silica is discrete as amorphous hydrous silica in allophane B. Fieldes could offer no satisfactory explanation as to why co-precipitation and linking of alumina and silica occur to only a limited extent in allophane B. He did not want to state that allophane B is simply a mixture of amorphous alumina and silica. Differential thermal analysis shows that a high temperature exotherm between 850° and 1000° C. is strong in allophane A, not present in allophane B, and weakly developed in the intermediate form, allophane AB. Fieldes (1955) has presented a weathering sequence of clays derived from rhyolitic and andesitic ash: allophane B—allophane AB—allophane A—meta-halloysite—kaolinite. He has stated that in this sequence the stable form is meta-halloysite and progress towards this stable form through allophane A is consistent with the mechanism proposed by Tamura and Jackson (1953). The structure consisting of hydrous alumina octahedra randomly cross-linked by silica tetrahedra and called allophane by Tamura and Jackson would hence correspond to allophane A as proposed by Fieldes.

There is a growing consensus among investigators in this field that amorphous colloids may play a very important role in soil formation and in establishing properties of many soils of the continental United States as well as in the Pacific islands. Because of their noncrystalline nature, identification of allophane and other amorphous constituents is at present very difficult, and at best very unreliable, by standard methods of analysis unless they be present as predominant components of their system. In view of the fact that transition from primary silicates (with the exception of micas) to the secondary layer silicates must include some solution and reprecipitation, it is reasonable to suspect that amorphous colloids exist, at least as a transition stage, in most of our soils. The extent of their presence is masked in most of our mineralogical studies by the crystalline components present.

The fact that amorphous colloids greatly affect properties of soils where they are dominant constituents emphasizes the need for more critical examination of our soils for evidence of their presence. According to Kanehiro and Sherman (1956), it is well established that allophane has low bulk density, high water-holding capacity, and, in some cases at least, a high cation exchange capacity. In addition it has been observed that allophane has a strong aggregation effect on soils, a very high phosphate fixing capacity, and the ability in some cases to fix organic compounds so as to render nitrogen available with difficulty to microorganisms and higher plants (T. Sudo, private communication).

Early researches of Burgess and McGeorge (1926) and Burgess (1929) in Arizona suggested that amorphous alumina, silica, or aluminosilicate may be formed quite readily in soils by application of alkaline solutions. Kerr (1928) further postulated that amorphous aluminosilicates may form even in slightly acid soils as a result of local hydrolysis of feldspars, solution of alkaline silicates and aluminates, and subsequent co-precipitation.

The Pacific region and its adjacent areas, with their recent volcanic materials offer a splendid opportunity for investigation of the presence of, the properties imparted by, and the mechanisms of formation of, such amorphous constituents in soils.

SUMMARY

The work on the amorphous mineral colloids of soils of the Pacific region and its nearby areas is described.

The amorphous colloids, especially allophane, dominate the clay fraction of many soils derived from volcanic ash, as well as some rocks, in the Pacific area. Soils dominated by these amorphous colloids have many distinct and unique properties. The position of the amorphous colloids, especially of allophane, in the weathering sequence remains to be fully clarified.

For many reasons, the identification of amorphous colloids is often difficult; however, recent improvements in instrumental techniques have greatly facilitated this identification.

REFERENCES

- AOMINE, S., and N. YOSHINAGA. 1955. Clay minerals of some well-drained volcanic ash soils in Japan. *Soil Sci.* 79: 349-358.
- AYRES, A. S. 1943. Soils of the high rainfall areas of the Hawaiian Islands. *Hawaii Agr. Expt. Sta. Tech. Bul.* 1.
- BATES, T. F. 1960. Rock weathering and clay formation in Hawaii. *Mineral Industries* 29: 1, 4-6.
- BIRRELL, K. S. 1952. Some physical properties of New Zealand volcanic ash soils. *Proc. of the First Australia-New Zealand Conf. on Soil Mech. and Foundation Eng.*
- BIRRELL, K. S., and M. FIELDDES. 1952. Allophane in volcanic ash soils. *Jour. of Soil Sci.* 3: 156-166.
- BIRRELL, K. S., and M. GRADWELL. 1956. Ion-exchange phenomena in some soils containing amorphous mineral constituents. *Jour. of Soil Sci.* 7: 130-147.
- BROWN, G. 1955. Report of the clay minerals group subcommittee on nomenclature of clay minerals. *Clay Min. Bul.* 2: 294-300.
- BURGESS, P. S. 1929. The so-called "build-up" and "break-down" of soil zeolites as influenced by reaction. *Arizona Agr. Exp. Sta. Tech. Bul.* 28: 101-135.
- BURGESS, P. S., and W. T. MCGEORGE. 1926. Zeolite formation in soils. *Science* 64: 652-653.
- DEAN, L. A. 1947. Differential thermal analysis of Hawaiian soils. *Soil Sci.* 63: 95-105.
- FIELDDES, M. 1955. Clay mineralogy of New Zealand soils, Part 2. Allophane and related mineral colloids. *N. Z. Jour. of Sci. and Tech.* 37: 336-350.
- . 1956. Clay mineralogy of New Zealand soils, Part 3. Infrared absorption spectra of soil clays. *N. Z. Jour. of Sci. and Tech.* 38: 31-43.
- . 1957. Clay mineralogy of New Zealand soils, Part 4. Differential thermal analysis. *N. Z. Jour. of Sci. and Tech.* 38: 533-570.

- FIELDER, M., and L. D. SWINDALE. 1954. Chemical weathering of silicates in soil formation. *N. Z. Jour. of Sci. and Tech.* 36: 140-154.
- FIELDER, M., L. D. SWINDALE, and J. P. RICHARDSON. 1952. Relation of colloidal hydrous oxides to the high cation-exchange capacity of some tropical soils of the Cook Islands. *Soil Sci.* 74: 197-205.
- FIELDER, M., and K. I. WILLIAMSON. 1955. Clay mineralogy of New Zealand soils, Part 1. Electron micrography. *N. Z. Jour. of Sci. and Tech.* 37: 314-335.
- GRIM, R. E. 1953. Clay mineralogy. McGraw-Hill Book Co., Inc., New York. 384 pp.
- JACKSON, M. L., S. A. TYLER, A. L. WILLIS, G. A. BOURBEAU, and R. P. PENNINGTON. 1948. Weathering sequence of clay-size minerals in soils and sediments, I. Fundamental generalizations. *Jour. of Phys. and Colloid Chem.* 52: 1237-1260.
- KANEHIRO, Y., and G. D. SHERMAN. 1956. Effect of dehydration-rehydration on cation exchange capacity of Hawaiian soils. *Soil Sci. Soc. Amer. Proc.* 20: 341-344.
- KELLEY, W. P., and J. B. PAGE. 1943. Criteria for the identification of the constituents of soil colloids. *Soil Sci. Soc. Amer. Proc.* 7: 175-181.
- KERR, H. W. 1928. The nature of base exchange and soil acidity. *Jour. Amer. Soc. Agron.* 20: 309-335.
- KERR, P. F. 1951. Reference Clay Minerals. Amer. Pet. Inst. Proj. 49. Columbia University, New York.
- MATSUSAKA, Y., and G. D. SHERMAN. 1961. Magnetism of iron oxide in Hawaiian soils. *Soil Sci.*: in press.
- ROSS, C. S., and P. F. KERR. 1934. Halloysite and allophane. *U.S. Geol. Surv. Prof. Paper* 185-G: 135-148.
- SHERMAN, G. D. 1957. Formation of gibbsite aggregates in latosols developed on volcanic ash. *Science* 125: 1243-1244.
- STROMEYER, F., and J. F. L. HAUSMANN. 1816. *Göttingische Gelehrte Anzeigen.* 2: 125.
- SUDO, T. 1954. Clay mineralogical aspects of the alteration of volcanic glass in Japan. *Clay Min. Bul.* 2: 96-106.
- SUDO, T., and J. OSSAKA. 1952. Hydrated halloysite from Japan. *Jap. Jour. of Geol. and Geog.* 22: 215-229.
- TAMURA, T., and M. L. JACKSON. 1953. Structural and energy relationships in the formation of iron and aluminum oxides, hydroxides, and silicates. *Science* 117: 381-385.
- TAMURA, T., M. L. JACKSON, and G. D. SHERMAN. 1953. Mineral content of low humic, humic and hydrol humic latosols of Hawaii. *Soil Sci. Soc. Amer. Proc.* 17: 343-346.
- . 1955. Mineral content of a latosolic brown forest soil and a humic ferruginous latosol of Hawaii. *Soil Sci. Soc. Amer. Proc.* 19: 435-439.
- TANADA, T. 1950. Certain properties of the inorganic colloidal fraction of Hawaiian soils. *Jour. of Soil Sci.* 2: 83-96.
- WHITTIG, L. D. 1954. Crystalline and amorphous weathering products in some soils of temperate and tropical origin. Thesis, Univ. of Wisconsin Library.
- WHITTIG, L. D., V. J. KILMER, R. C. ROBERTS, and J. G. CADY. 1957. Characteristics and genesis of Cascade and Powell soils of northwestern Oregon. *Soil Sci. Soc. Amer. Proc.* 21: 226-232.